

[Document's name] Specification

[Title of the invention] Membrane-electrode structure

[Claim 1]

A membrane-electrode structure comprising a pair of  
5 electrodes that comprise catalyst layers, and a solid  
polymer electrolyte membrane sandwiched by said catalyst  
layers of both electrodes, characterized in that:

said catalyst layers are positioned in the inner  
circumference side than the outer circumferential edge of  
10 said solid polymer electrolyte membrane;

at least one face of said solid polymer electrolyte  
membrane is coated with said catalyst layers, and an  
adhesive support layer that is formed on said catalyst  
layers and throughout the entire circumference of the outer  
15 circumferential side of said catalyst layers, adheres to  
said solid polymer electrolyte membrane, and supports said  
solid polymer electrolyte membrane; and

said adhesive support layer is formed of an adhesive  
having fluorine atoms in the molecular structure.

20 [Claim 2]

The membrane-electrode structure according to claim 1,  
characterized in that said adhesive has a tensile  
elongation at break of 150% or more after curing.

[Claim 3]

25 The membrane-electrode structure according to claim 1  
or 2, characterized in that said adhesive contains a  
polysiloxane compound and a molecule that has at least two

alkenyl groups.

[Claim 4]

The membrane-electrode structure according to any one of claims 1 through 3, characterized in comprising a  
5 diffusion layer that coats said catalyst layers and said adhesive support layer.

[Claim 5]

The membrane-electrode structure according to any one of claims 1 through 4, characterized in that at least a  
10 part of the outer circumferential edge of said one catalyst layer is positioned on the portion different from the outer circumferential edge of the other catalyst layer, with sandwiching said solid polymer electrolyte membrane.

[Claim 6]

15 The membrane-electrode structure according to claim 5, characterized in that the outer circumferential edge of said one catalyst layer is positioned in the inner circumference side than the outer circumferential edge of the other catalyst layer, with sandwiching said solid  
20 polymer electrolyte membrane.

[Detailed Description of the Invention]

[0001]

[Technical field]

The present invention relates to a membrane-electrode  
25 structure that is used in polymer electrolyte fuel cells.

[0002]

[Background art]

The petroleum source has been exhausted, and at the same time, environmental problems such as global warming due to the consumption of fossil fuel have increasingly become serious. Thus, a fuel cell receives attention as a  
5 clean power source for electric motors that is not accompanied with the generation of carbon dioxide. The above fuel cell has been widely developed, and some fuel cells have become commercially practical. When the above fuel cell is mounted in vehicles and the like, a polymer  
10 electrolyte fuel cell comprising a polymer electrolyte membrane is preferably used because it easily provides a high voltage and a large electric current.

[0003]

A membrane-electrode structure as shown in FIG. 4 has  
15 been known as a membrane-electrode structure used for the above polymer electrolyte fuel cell (refer to e.g., Patent Document 1).

[0004]

The membrane-electrode structure 12 shown in FIG. 4  
20 consists of a polymer electrolyte membrane 2, a pair of catalyst layers 3 and 4 that sandwich the polymer electrolyte membrane 2, and a pair of diffusion layers 5 and 6 that are laminated on both catalyst layers 3 and 4. In the membrane-electrode structure 12, the catalyst layers  
25 3 and 4, and the diffusion layers 5 and 6 are formed in the same size as the polymer electrolyte membrane 2, and are laminated so that the outer circumferential edge of each

layer 3, 4, 5, and 6 is aligned with the outer circumferential edge of the polymer electrolyte membrane 2.  
[0005]

5 In the membrane-electrode structure 12, when a reducing gas, such as hydrogen and methanol, is introduced through a diffusion layer 5 to a catalyst layer 3, protons formed in the catalyst layer 3 move to the catalyst layer 4, which is in the oxygen electrode side through the polymer electrolyte membrane 2. In the catalyst layer 4, an  
10 oxidizing gas, such as air and oxygen, is introduced through the diffusion layer 6, and the protons react with oxygen and electrons to form water. Therefore, by connecting the catalyst layers 3 and 4 with a conducting wire, the membrane-electrode structure 12 can be used as a  
15 fuel cell.  
[0006]

However, as FIG. 4 shows, if the catalyst layers 3 and 4 and the diffusion layers 5 and 6 are laminated so that the outer circumferential edges thereof are aligned  
20 with the outer circumferential edge of the polymer electrolyte membrane 2, there is a problem that the gas supplied to each of the diffusion layers 5 and 6 goes around the outer circumferential edge of the polymer electrolyte membrane 2 to the opposite side, and is mixed  
25 to each other. In addition, since the locations of the outer circumferential edges of the catalyst layers 3 and 4 are close to each other, there is a problem that the

catalyst layers 3 and 4 may be electrically short-circuited.  
[0007]

5 In order to solve the above-described problems, there  
has been proposed a membrane-electrode structure 13 wherein  
a polymer electrolyte membrane 2 is formed to be larger  
than catalyst layers 3 and 4 and diffusion layers 5 and 6,  
and the catalyst layers 3 and 4 and the diffusion layers 5  
and 6 are laminated so as to make their outer  
circumferential edges locate in the inner circumference  
10 side than the outer circumferential edge of the polymer  
electrolyte membrane 2, as FIG. 5 shows (refer to e.g.,  
Patent Document 2).

[0008]

15 According to the membrane-electrode structure 13 of  
the above, the gas supplied to each of diffusion layers 5  
and 6 is blocked by the portion of the polymer electrolyte  
membrane 2 exposed from the outer circumferential edges of  
the catalyst layers 3 and 4 and the diffusion layers 5 and  
6 to prevent the mixing thereof. The above-described  
20 exposed portion of the polymer electrolyte membrane 2 can  
also prevent the electrical short-circuiting of the  
catalyst layers 3 and 4.

[0009]

25 However, in a fuel cell using the membrane-electrode  
structure 13, if the thickness of the polymer electrolyte  
membrane 2 is thinned for improving the output, the  
mechanical strength of the polymer electrolyte membrane 2

is lowered, and the portion exposed from the outer circumferential edges of the catalyst layers 3 and 4 and the diffusion layers 5 and 6 is easily broken. Therefore, the present applicant has proposed membrane-electrode structures 1a and 1b wherein the entire outer circumference of one catalyst layer 4 is adhered to the polymer electrolyte membrane 2 to form an adhesive support layer 9 for supporting the polymer electrolyte membrane 2, and one face of the polymer electrolyte membrane 2 is coated with the catalyst layer 4 and the adhesive support layer 9, as FIGS. 1 and 2 shows (refer to Japanese Patent Laid-Open No. 2001-260240).

[0010]

In the membrane-electrode structures 1a and 1b, the polymer electrolyte membrane 2 extended outwardly from the outer circumferential edges of the catalyst layers 3 and 4 and the diffusion layers 5 and 6 is protected by the adhesive support layer 9, and the prevention of damage is expected. Also in the membrane-electrode structures 1a and 1b, by forming a diffusion layer 6 that coats the catalyst layer 4 and the adhesive support layer 9, it is expected that the function to protect the above-described polymer electrolyte membrane 2 can be strengthened.

[0011]

However, since a fuel cell is exposed to a high-temperature high-humidity environment during operation, the adhesive support layer 9 may peel off the polymer

electrolyte membrane 2 depending on the type of adhesive that constitutes the adhesive support layer 9 of the membrane-electrode structures 1a and 1b, and the effect to protect the polymer electrolyte membrane 2 may not be sufficiently achieved.

[0012]

[Patent Document 1]

U.S. Pat. No. 5,176,966

[Patent Document 2]

Japanese Patent Laid-Open No. 2000-223136

[0013]

[Problems to be solved by the invention]

It is an object of the present invention to solve the above-described problems, and to provide a membrane-electrode structure comprising an adhesive support layer that does not peel off the solid polymer electrolyte membrane even in a high-temperature high-humidity environment during the operation of a fuel cell.

[0014]

[Means for solving the problem]

To achieve the above objects, the membrane-electrode structure of the present invention is characterized in comprising a pair of electrodes each having a catalyst layer, and a solid polymer electrolyte membrane sandwiched by the catalyst layers of both electrodes, wherein the catalyst layers are positioned in the inner circumference side than the outer circumferential edge of the solid

polymer electrolyte membrane; at least one face of the solid polymer electrolyte membrane is coated with the catalyst layers, and an adhesive support layer that is formed on the catalyst layers and throughout the entire circumference of the outer circumferential side of the catalyst layers, adheres to the solid polymer electrolyte membrane, and supports the solid polymer electrolyte membrane; and the adhesive support layer is formed of an adhesive having fluorine atoms in the molecular structure.

[0015]

According to the membrane-electrode structure of the present invention, since the adhesive support layer is formed of an adhesive having fluorine atoms in the molecular structure, it can strongly adhere to the solid polymer electrode membrane and does not peel off, even if it is exposed to a high-temperature high-humidity environment during the operation of the fuel cell. Therefore, it can protect the solid polymer electrolyte membrane extended outwardly from the outer circumferential edges of the catalyst layers and can prevent the damage thereof. The adhesive support layer may be formed on only one face of the solid polymer electrolyte membrane or may be formed on both faces thereof.

[0016]

On the other hand, if the adhesive support layer strongly adheres to the solid polymer electrolyte membrane, when the solid polymer electrolyte membrane repeats



expansion and shrinkage in the above-described high-temperature high-humidity environment, the adhesive support layer may not be able to follow the above-described expansion and shrinkage. In such a case, the solid polymer electrolyte membrane may be restricted from expansion and shrinkage in the vicinity of the edge portion of the adhesive support layer to produce the concentration of stress and may be damaged. Therefore, in the membrane-electrode structure of the present invention, the above-described adhesive after curing is characterized in having a tensile elongation at break of 150% or more.

[0017]

According to the adhesive support layer formed of such an adhesive, since the adhesive has a tensile elongation at break of 150% or more, the adhesive support layer can follow the expansion and shrinkage of the solid polymer electrolyte membrane in the high-temperature high-humidity environment, and can relax the concentration of stress of the solid polymer electrolyte membrane in the edge portion thereof to prevent damage.

[0018]

Examples of the adhesives include adhesives that contain a polysiloxane compound and a molecule containing at least two alkenyl groups. The adhesives are cured by the cross-linking of the alkenyl groups and the polysiloxane compound.

[0019]

Examples of the alkenyl groups include univalent unsaturated aliphatic groups such as vinyl, allyl, and butenyl groups. The polysiloxane compound and the molecule containing alkenyl groups may be molecules independent from each other, or may be a polysiloxane compound having the alkenyl groups within the same molecule that cures by the cross-linking reaction in molecules.

[0020]

The membrane-electrode structure of the present invention is characterized in comprising a diffusion layer that coats the catalyst layers and the adhesive support layer. The catalyst layers and the adhesive support layer are reinforced by the coating of the catalyst layers and the adhesive support layer by the diffusion layer, and the solid polymer electrolyte membrane extended outwardly from the outer circumferential edge of the catalyst layers is further strongly protected.

[0021]

In the membrane-electrode structure having the above-described constitution, if the outer circumferential edges of the pair of catalyst layers are positioned so as to align to each other sandwiching the solid polymer electrolyte membrane, stress due to the catalyst layers is concentrated on the same positions on the front and back of the solid polymer electrolyte membrane when a fuel cell is formed. As a result, there is large possibility that the solid polymer electrolyte membrane is broken at the portion

sandwiched by the outer circumferential edges of the pair of catalyst layers.

[0022]

Therefore, the membrane-electrode structure of the present invention is characterized in that at least a part of the outer circumferential edge of one catalyst layer positions at the portion different from the outer circumferential edge of the other catalyst layer, with sandwiching the solid polymer electrolyte membrane. According to the above-described constitution, the stress due to outer circumferential edges of the catalyst layers can be dissipated on both the front and back of the solid polymer electrolyte membrane, and the damage of the solid polymer electrolyte membrane can be prevented.

[0023]

To dissipate the stress, it is preferable that the outer circumferential edge of one catalyst layer is positioned in the inner circumferential side than the outer circumferential edge of the other catalyst layer, with sandwiching the solid polymer electrolyte membrane.

[0024]

[Best Mode for Carrying Out the Invention]

Next, the first embodiment of the present invention will be described with reference to accompanying drawings. FIG. 1 is an explanatory sectional view showing a constitution example of the membrane-electrode structure of the first embodiment, FIG. 2 is an explanatory sectional

view showing another constitution example of the membrane-electrode structure of the first embodiment, and FIG. 3 is an explanatory sectional view showing the constitution of a membrane-electrode structure used in the measurement of the adhesive strength of the adhesive support layer, and in the test for examining the stress concentration in the vicinity of the edge portion of the adhesive support layer.

[0025]

As FIG. 1 shows, the membrane-electrode structure 1a comprises a solid polymer electrolyte membrane 2, a pair of catalyst layers 3 and 4 that sandwich the solid polymer electrolyte membrane 2, and a pair of diffusion layers 5 and 6 laminated on both the catalyst layers 3 and 4. In the membrane-electrode structure 1a, a catalyst layer 3 and a diffusion layer 5 form an electrode 7; and a catalyst layer 4 and a diffusion layer 6 form an electrode 8.

[0026]

The solid polymer electrolyte membrane 2 is formed to be larger than the catalyst layers 3 and 4, and the catalyst layers 3 and 4 are laminated to position in the inner circumference side than the outer circumferential edge of the solid polymer electrolyte membrane 2. One face of the solid polymer electrolyte membrane 2 is coated with a catalyst layer 4 formed on the entire outer circumference side of the catalyst layer 4, and an adhesive support layer 9 that is adhered to the solid polymer electrolyte membrane 2 and supports the solid polymer electrolyte membrane 2.

The catalyst layer 4 and the adhesive support layer 9 are coated with the diffusion layers 6. On the other face of the solid polymer electrolyte membrane 2, the portion that extends outwardly from the outer circumferential edge of the catalyst layer 3 is exposed.

[0027]

In the membrane-electrode structure 1a, the catalyst layer 3 is formed to be larger than the catalyst layer 4, and the outer circumferential edge of the catalyst layer 4 is positioned in the inner circumference side than the outer circumferential edge of the catalyst layer 3, with sandwiching the solid polymer electrolyte membrane 2. However, as the membrane-electrode structure 1b shown in FIG. 2, the catalyst layer 4 may be formed to be larger than the catalyst layer 3, and the outer circumferential edge of the catalyst layer 3 may be positioned in the inner circumference side than the outer circumferential edge of the catalyst layer 4, with sandwiching the solid polymer electrolyte membrane 2.

[0028]

The solid polymer electrolyte membrane 2 is formed of a polymer electrolyte such as a perfluoroalkylene sulfonic acid polymer compound (e.g., Nafion (trade name) manufactured by DuPont) and a sulfonated polyarylene compound, and has a dry membrane thickness of, for example, 50  $\mu\text{m}$ .

[0029]

The catalyst layers 3 and 4 are formed of catalyst particles and an ion-conductive binder. As the catalyst particles, for example, platinum particles supported by carbon black (furnace black) so that platinum: carbon particles=1:1 (ratio by weight), are used. As the ion-conductive binder, the above-described polymer electrolyte is used.

[0030]

The diffusion layers 5 and 6 are formed of carbon paper and a backing layer (not shown) on the carbon paper. The backing layer is, for example, a 4:6 (ratio by weight) mixture of carbon black and polytetrafluoroethylene particles, and the catalyst layers 3 and 4 are formed on the backing layer.

[0031]

The adhesive support layer 9 is formed of an adhesive that has fluorine atoms in the molecular structure thereof. It is preferable that the adhesive contains a polysiloxane compound and a molecule that has at least two alkenyl groups, and cures when the alkenyl groups cross-link with the polysiloxane compound. It is also preferable that the adhesive has a tensile elongation at break of 150% or more after curing.

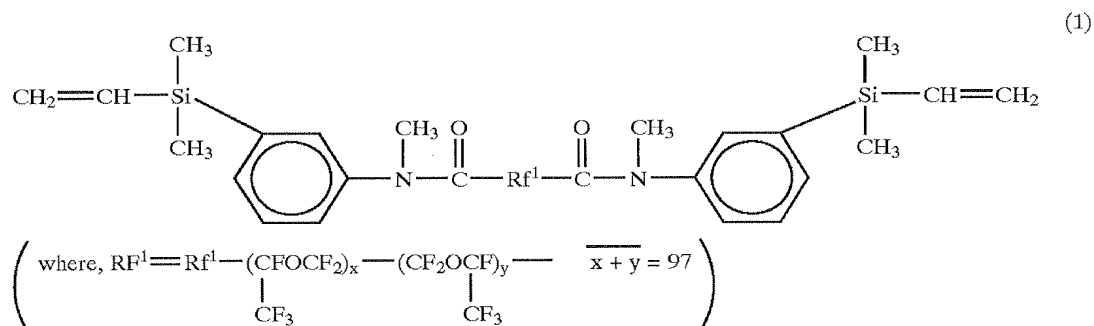
[0032]

Examples of such adhesives include an adhesive produced by mixing and agitating 100 parts of the polymer represented by the following formula (1) (viscosity: 4.4

Pa.s; average molecular weight: 16,500; quantity of vinyl groups: 0.012 mol/100 g); 4 parts by weight of organo-hydrogen polysiloxane (CR-100 (trade name) manufactured by Kaneka Corporation); 8 parts of a plasticizer (PAO-5010 (trade name) manufactured by Idemitsu Petrochemical Co., Ltd.); 12 parts of fumed silica (manufactured by Tosoh Silica Corporation); and 3 parts of organo-silane (KBM-303 (trade name) manufactured by Shin-Etsu Chemical Co., Ltd.); and defoaming; to which bis(1,3-divinyl-1,1,3-tetramethyl disiloxane)-platinum catalyst is added as a reaction catalyst so that the content of platinum is  $5 \times 10^{-4}$  equivalent weights to the number of moles of the vinyl groups in the polymer represented by the following formula (1).

[0033]

[Formula 1]



[0034]

Alternatively, another example of such adhesives is an adhesive produced by mixing and agitating 100 parts of methyl(3,3,3-trifluoropropyl)polysiloxane of which both

ends of the molecular chain are blocked by dimethylvinylsiloxyl groups (viscosity: 1.0 Pa·s; content of vinyl groups bonded to silicon atoms: 1.0% by weight); 3.5 parts of dimethylhydrogensiloxyl(3,3,3-trifluoropropyl)polysiloxane of which both ends of the molecular chain are blocked by dimethylhydrogensiloxyl groups (viscosity: 0.01 Pa·s; content of vinyl groups bonded to silicon atoms: 0.5% by weight); and 0.01 parts of ferrocene; and defoaming; to which bis(1,3-divinyl-1,1,3-tetramethyl disiloxane)-platinum catalyst is added as a reaction catalyst so that the ratio by weight of platinum to methyl(3,3,3-trifluoropropyl) polysiloxane of which both ends of the molecular chain are blocked by dimethylvinylsiloxyl groups is 5 ppm.

[0035]

In FIGS. 1 and 2, although the edge of the catalyst layer 4 and the edge of the adhesive support layer 9 are formed in close contact to each other, the adhesive support layer 9 may be formed on the entire circumference side of the catalyst layer 4, and a gap may be formed between the edge of the catalyst layer 4 and the edge of the adhesive support layer 9. Also in FIGS. 1 to 4, although the diffusion layer 5 of the same size as the catalyst layer 3 is laminated on the catalyst layer 3 on the face opposite to the face where the adhesive support layer 9 is formed, the diffusion layer 5 may be larger than the catalyst layer 3, and may have, for example, the same as the diffusion



layers 2.

[0036]

Furthermore, in FIGS. 1 and 2, although only one face of the solid polymer electrolyte membrane 2 is coated with the catalyst layer 4 and the adhesive support layer 9, the  
5 adhesive support layer 9 may be formed throughout the entire outer circumference side of the catalyst layer 3 on the other face, which may be coated with the catalyst layer 3 and the adhesive support layer 9. In this case, the  
10 adhesive support layer 9 may coat at least a part of the solid polymer electrolyte membrane 2 extended outwardly from the outer circumferential edge of the catalyst layer 3, and is not required to coat the entire face.

[0037]

15 In the membrane-electrode structures 1a and 1b, the electrode 7 is made to be a fuel electrode (anode), and a reducing gas such as hydrogen and methanol is introduced into the catalyst layer 3 through the diffusion layer 5; on the other hand, the electrode 8 is made to be an oxygen  
20 electrode (cathode), and an oxidizing gas such as air and oxygen is introduced into the catalyst layer 4 through the diffusion layer 6. By doing so, in the fuel electrode (electrode 7) side, protons and electrons are produced from the reducing gas by the action of the catalyst contained in  
25 the catalyst layer 3, and the protons move to the catalyst layer 4 in the oxygen electrode (electrode 8) side via the solid polymer electrolyte membrane 2. The protons react

with the oxidizing gas and electrons introduced into the catalyst layer 4 to form water by the action of the catalyst contained in the catalyst layer 4. Therefore, by connecting the fuel electrode to the oxygen electrode through a conductive wire, a circuit for transporting the electrons produced in the fuel electrode to the oxygen electrode is formed to abstract electric current, and the membrane-electrode structures 1a and 1b can be used as a fuel cell.

[0038]

Next, Examples and Comparative Examples will be shown.

[0039]

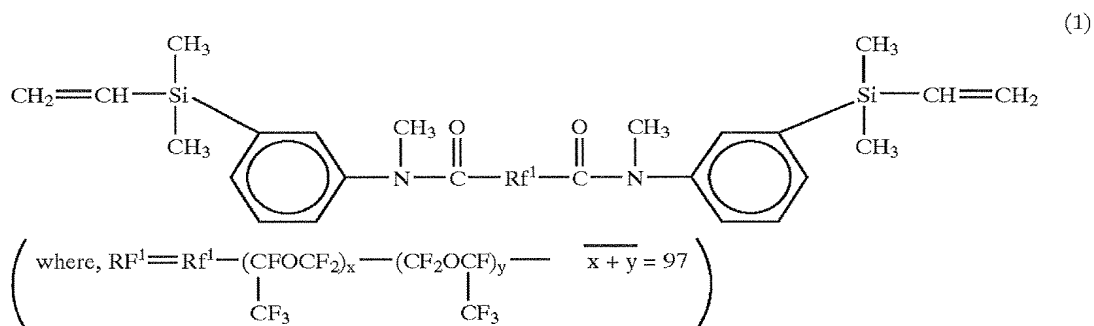
[EXAMPLE 1]

In this example, an adhesive was first prepared by mixing and agitating 100 parts of the polymer represented by the following formula (1) (viscosity: 4.4 Pa•s; average molecular weight: 16,500; quantity of vinyl groups: 0.012 mol/100 g); 4 parts by weight of organo-hydrogen polysiloxane (CR-100 (trade name) manufactured by Kaneka Corporation); 8 parts of a plasticizer (PAO-5010 (trade name) manufactured by Idemitsu Petrochemical Co., Ltd.); 12 parts of fumed silica (manufactured by Tosoh Silica Corporation); and 3 parts of organo-silane (KBM-303 (trade name) manufactured by Shin-Etsu Chemical Co., Ltd.); defoaming; and adding a xylene solution ( $8.3 \times 10^{-5}$  mol/ $\mu$ l) of bis(1,3-divinyl-1,1,3-tetramethyl disiloxane)-platinum catalyst as a reaction catalyst so that the content of

platinum is  $5 \cdot 10^{-4}$  equivalent weights to the number of moles of the vinyl groups in the polymer represented by the following formula (1).

[0040]

5 [Formula 2]



[0041]

10 The tensile elongation at break of the above-described adhesive, measured in accordance with JIS K 6301 was 210%.

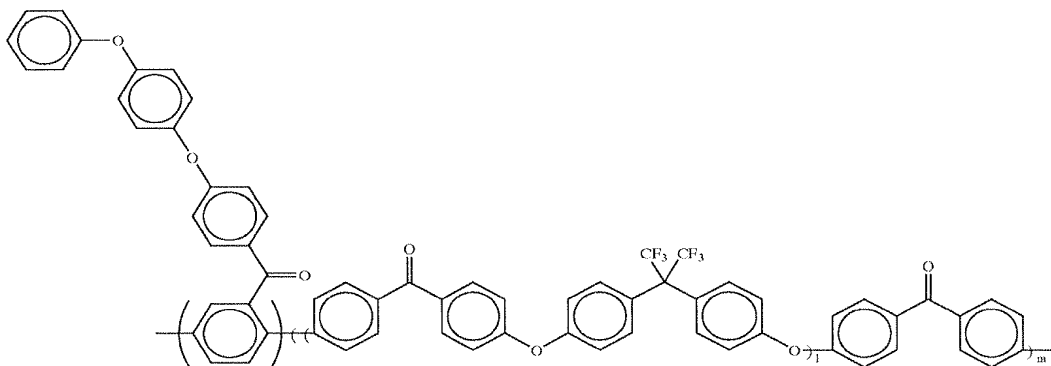
[0042]

15 Next, a sulfonated polyarylene compound sulfonated so as to have ion-exchange capacity of 2.0 meq/g was prepared by adding concentrated sulfuric acid to a polyarylene compound represented by the following formula (2).

[0043]

[Formula 3]

(2)



$$n:m = 1:1$$

[0044]

Next, the sulfonated polyarylene compound was dissolved in N-methylpyrrolidone to prepare a polymer electrolyte solution, a membrane was formed from the polymer electrolyte solution by the casting method, and the membrane was dried to prepare a solid polymer electrolyte membrane 2 of a dry membrane thickness of 50  $\mu\text{m}$ .

[0045]

Next, platinum particles were supported by carbon black (furnace black) at a weight ratio of carbon black:platinum=1:1 to prepare catalyst particles. Next, the catalyst particles were evenly dispersed in a solution of perfluoroalkylene sulfonic acid polymer as a ion-conductive polymer binder solution (e.g., Nafion (trade name) manufactured by DuPont) at a weight ratio of catalyst particles:binder solution=1:1 to prepare a catalyst paste.

[0046]

Next, a slurry prepared by evenly dispersing the

mixture obtained by mixing carbon black and polytetrafluoroethylene (PTFE) particles at a weight ratio of 4:6 in ethylene glycol was applied onto a side of carbon paper and dried to form a backing layer, and a diffusion layers 5 and 6 consisting of the carbon paper and the backing layer were formed. The diffusion layer 5 had a size within the size of the inner circumference side of the outer circumferential edge of the solid polymer electrolyte membrane 2, and the diffusion layer 6 had a size same as the size of the solid polymer electrolyte membrane 2.

[0047]

Next, the catalyst paste was applied onto the entire surface of the backing layer of the diffusion layer 5 by screen printing so that the platinum content becomes 0.5 mg/cm<sup>2</sup>, heated at 60°C for 10 minutes, heated under a reduced pressure at 120°C for 15 minutes, and dried to form a catalyst layer 3.

[0048]

Next, the adhesive was applied to the entire circumference of the portion to be the outer circumference side of the catalyst layer 4 of the diffusion layer 6 to form an adhesive support layer 9. Next, the catalyst paste was applied onto the inner circumference side of the adhesive support layer 9 formed on the diffusion layer 6 by screen printing so that the platinum content becomes 0.5 mg/cm<sup>2</sup>, heated at 60°C for 10 minutes, heated under a reduced pressure at 120°C for 15 minutes, and dried to form

a catalyst layer 4. The catalyst layer 4 had a size within the inner circumference side of the outer circumferential edge of the catalyst layer 3.

[0049]

5           Next, the solid polymer electrolyte membrane 2 was sandwiched between the catalyst layers 3 and 4, and integrated with the catalyst layers 3 and 4 by hot-pressing at 150°C and 2.5 MPa for 15 minutes to produce a membrane-electrode structure 1a shown in FIG. 1.

10          [0050]

          Next, in order to be used for the measurement of the adhesive strength of the adhesive support layer 9 and the test for examining the stress concentration of the solid polymer electrolyte membrane 2 in the vicinity of the edge portion of the adhesive support layer 9, a membrane-electrode structure 11 shown in FIG. 3 was produced. The membrane-electrode structure 11 has the same constitution as the membrane-electrode structure 1a other than the following aspects:

20           (1) The catalyst layers 3 and 4 have the same size, and are laminated so that the outer circumferential edges are aligned to each other, with sandwiching the solid polymer electrolyte membrane 2.

          (2) The diffusion layer 5 is extended outwardly from the outer circumferential edge of the catalyst layer 3.

25           (3) The solid polymer electrolyte membrane 2 and the diffusion layer 6 are extended outwardly from the outer

circumferential edge of the adhesive support layer 9.

(4) A gap 10 is formed between the edge of the catalyst layer 4 and the edge of the adhesive support layer 9.

5 [0051]

Next, after allowing the membrane-electrode structure 11 to stand in an environment of 23°C and a relative humidity of 30% for 100 hours, only the carbon paper peeled off the diffusion layer 5, and cut into a strip of a width 10 of 1 cm in the cross-sectional direction to prepare a test piece.

[0052]

Next, the ends of the solid polymer electrolyte membrane 2 extended outwardly from the outer 15 circumferential edge of the adhesive support layer 9 and the diffusion layer 6 were held, and were pulled in directions opposite to each other at a speed of 1 mm/sec to measure the load when the adhesive support layer 9 peeled off as the peel strength. The measurements were carried out 20 for 5 test pieces, and the mean value was calculated as the initial strength. The results are shown in Table 1.

[0053]

Next, considering a high-temperature high-humidity environment during the operation of the fuel cell, the test 25 piece was held between punching sheets made of polytetrafluoroethylene, and the cycles of the operations to immerse the test piece in water of 95°C for 5 hours

applying a load of a surface pressure of 490 kPa, and to dry it at 100°C for 5 hours, were repeated. After each of 10, 50, 100, and 200 cycles of the above operations, the peel strength of the test piece was obtained in the same manner as in the above-described initial strength. The results are shown in Table 1.

[0054]

Also after each of 10, 50, 100, and 200 cycles of the above operations, the presence of cracks in the portion facing the gap 8 of the solid polymer electrolyte membrane 2 and the portion in the vicinity of the outer circumferential edge of the adhesive support layer 9 was observed through an optical microscope and a scanning electron microscope to use the results as an index of stress concentration after each cycle. The more the cracks in the above portions, the larger the stress concentration. The results are shown in Table 2.

[0055]

[EXAMPLE 2]

In this example, an adhesive was prepared in the same manner as in Example 1 except that the quantity of compounded fumed silica was 20 parts. The tensile elongation at break after curing of the above adhesive measured in the same manner as in Example 1 was 150%.

[0056]

Next, a membrane-electrode structure 1a shown in FIG. 1 and a membrane-electrode structure 11 shown in FIG. 3



were produced in the same manner as in Example 1 except that the above-mentioned adhesive was used in place of the adhesive used in Example 1, and the stress concentration of the solid polymer electrolyte membrane 2 was examined in the same manner as in Example 1. The results are shown in Table 2.

[0057]

[EXAMPLE 3]

In this example, an adhesive was produced by mixing and agitating 100 parts of methyl (3,3,3-trifluoropropyl) polysiloxane of which both ends of the molecular chain are blocked by dimethylvinylsiloxo groups (viscosity: 1.0 Pa•s; content of vinyl groups bonded to silicon atoms: 1.0% by weight); 3.5 parts of dimethylhydrogensiloxo(3,3,3-trifluoropropyl)polysiloxane of which both ends of the molecular chain are blocked by dimethylhydrogensiloxo groups (viscosity: 0.01 Pa•s; content of vinyl groups bonded to silicon atoms: 0.5% by weight); and 0.01 parts of ferrocene; and defoaming; to which a xylene solution ( $8.3 \times 10^{-5}$  mol/ $\mu$ l) of bis(1,3-divinyl-1,1-tetramethyl disiloxane)-platinum catalyst was added as a reaction catalyst so that the ratio by weight of platinum to methyl(3,3,3-trifluoropropyl)polysiloxane of which both ends of the molecular chain are blocked by dimethylvinylsiloxo groups was 5 ppm. The tensile elongation at break after curing of the above adhesive measured in the same manner as in Example 1 was 250%.

[0058]

Next, a membrane-electrode structure 1a shown in FIG. 1 and a membrane-electrode structure 11 shown in FIG. 3 were produced in the same manner as in Example 1 except that the above-mentioned adhesive was used in place of the adhesive used in Example 1, and the peel strength of the adhesive support layer 9 was measured in the same manner as in Example 1. The results are shown in Table 1.

[0059]

The stress concentration of the solid polymer electrolyte membrane 2 was examined in the same manner as in Example 1. The results are shown in Table 2.

[0060]

[COMPARATIVE EXAMPLE 1]

In this comparative example, an adhesive was prepared in the same manner as in Example 1 except that an isobutylene resin that contains no fluorine atoms in the molecule thereof (Epion (trade name) manufactured by Kaneka Corporation) was used in place of the polymer represented by the formula (1).

[0061]

Next, a membrane-electrode structure 1a shown in FIG. 1 and a membrane-electrode structure 11 shown in FIG. 3 were produced in the same manner as in Example 1 except that the adhesive prepared in this example was used in place of the adhesive used in Example 1, and the peel strength of the adhesive support layer 9 was measured in

the same manner as in Example 1. The results are shown in Table 1.

[0062]

[COMPARATIVE EXAMPLE 2]

5           In this comparative example, a membrane-electrode structure 1a shown in FIG. 1 and a membrane-electrode structure 11 shown in FIG. 3 were produced in the same manner as in Example 1 except that a silicone-based adhesive not containing fluorine atoms in the molecule  
10       (1209 (trade name) manufactured by Three Bond Co., Ltd.) was used in place of the adhesive used in Example 1, and the adhesive support layer 9 was measured in the same manner as in Example 1. The results are shown in Table 1.

[0063]

15       [COMPARATIVE EXAMPLE 3]

          In this comparative example, a membrane-electrode structure 1a shown in FIG. 1 and a membrane-electrode structure 11 shown in FIG. 3 were produced in the same manner as in Example 1 except that a silicone-based  
20       adhesive not containing fluorine atoms in the molecule (1211 (trade name) manufactured by Three Bond Co., Ltd.) was used in place of the adhesive used in Example 1, and the adhesive support layer 9 was measured in the same manner as in Example 1. The results are shown in Table 1.

25       [0064]

[COMPARATIVE EXAMPLE 4]

          In this comparative example, an adhesive was prepared

in the same manner as in Example 1 except that the quantity of compounded fumed silica was 30 parts. The tensile elongation at break after curing of the above adhesive measured in the same manner as in Example 1 was 120%.

5 [0065]

Next, the a membrane-electrode structure 1a shown in FIG. 1 and a membrane-electrode structure 11 shown in FIG. 3 were produced in the same manner as in Example 1 except that the adhesive prepared in this comparative example was used in place of the adhesive used in Example 1, and the stress concentration of the solid polymer electrolyte membrane 2 was examined in the same manner as in Example 1. The results are shown in Table 2.

[0066]

15 [COMPARATIVE EXAMPLE 5]

In this comparative example, an adhesive was prepared in the same manner as in Example 1 except that the quantity of compounded fumed silica was 40 parts. The tensile elongation at break after curing of the above adhesive measured in the same manner as in Example 1 was 90%.

[0067]

Next, the a membrane-electrode structure 1a shown in FIG. 1 and a membrane-electrode structure 11 shown in FIG. 3 were produced in the same manner as in Example 1 except that the adhesive prepared in this comparative example was used in place of the adhesive used in Example 1, and the stress concentration of the solid polymer electrolyte

membrane 2 was examined in the same manner as in Example 1.  
The results are shown in Table 2.

[0068]

[Table 1]

**TABLE 1**

	<u>Peel strength of adhesive support layer 9 (gf/cm)</u>				
	Exam- ple 1	Exam- ple 3	Comparative Example 1	Comparative Example 2	Comparative Example 3
Initial strength	158	122	52	31	84
After 10 cycles	141	101	Peeled off	Peeled off	40
After 50 cycles	131	90	Peeled off	Peeled off	Peeled off
After 100 cycles	117	83	Peeled off	Peeled off	Peeled off
After 200 cycles	98	75	Peeled off	Peeled off	Peeled off

[0069]

[Table 2]

**TABLE 2**

	<u>Tensile elongation at break of adhesive support layer 9 after curing, and presence of cracks of solid polymer electrolyte membrane 2</u>				
	Example 1	Exam- ple 2	Exam- ple 3	Comparative Example 4	Comparative Example 5
Tensile elongation at break (%)	210	150	250	120	90
After 10 cycles	o	o	o	o	o
After 50 cycles	o	o	o	o	x
After 100 cycles	o	o	o	x	x
After 200 cycles	o	o	o	x	x

o: Cracked

x: Not cracked

[0070]

It is obvious from Table 1 that the adhesive support layer 9 consisting of an adhesive that contains fluorine molecules in the molecules thereof (Examples 1 and 3) has a high peel strength even after the treatments assuming a high-temperature high-humidity environment during the operation of the fuel cell are repeated for 200 cycles, and a high adhesive strength can be obtained. Whereas, it is obvious that the adhesive support layer 9 consisting of an adhesive that contains no fluorine molecules in the molecules thereof (Comparative Examples 1 to 3) has a low initial peel strength, and easily peels off by the above-described, and sufficient adhesive strength cannot be obtained.

[0071]

It is also obvious from Table 2 that when the adhesive support layer 9 consisting of the adhesive that has the tensile elongation at break is 150% or more after curing is used (Examples 1 to 3), no cracks were observed in the solid polymer electrolyte membrane 2 even after the treatments assuming a high-temperature high-humidity environment during the operation of the fuel cell are repeated for 200 cycles, and stress concentration is relaxed. Whereas, it is obvious that when the adhesive support layer 9 consisting of the adhesive that has the tensile elongation at break is less than 150% after curing is used (Comparative Examples 4 and 5), the solid polymer electrolyte membrane 2 is easily cracked, and stress

concentration cannot be relaxed.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[FIG. 1]

An explanatory sectional view showing a constitution  
5 example of the membrane-electrode structure of the first  
embodiment.

[FIG. 2]

An explanatory sectional view showing another  
constitution example of the membrane-electrode structure of  
10 the first embodiment.

[FIG. 3]

An explanatory sectional view showing the  
constitution of a membrane-electrode structure used in the  
measurement of the adhesive strength of the adhesive  
15 support layer, and in the test for examining the stress  
concentration in the vicinity of the edge portion of the  
adhesive support layer.

[FIG. 4]

An explanatory sectional view showing a constitution  
20 example of a conventional membrane-electrode structure.

[FIG. 5]

An explanatory sectional view showing a constitution  
example of another conventional membrane-electrode  
structure.

25 [References]

1a, 1b: membrane-electrode structure; 2: solid polymer  
electrolyte membrane; 3, 4: catalyst layer; 5, 6: diffusion

layer; 7: adhesive support layer